Research and Development

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### **Project Summary**

## Ground Water—Mineralogy Relationship for *In Situ* Oil Shale Retorting

J.J. Fitzpatrick

Potential ground water problems associated with modified in situ (MIS) oil shale retorting need to be examined in order to minimize or mitigate possible invasion of spent shale leachates into ground water reservoirs in actively mined or mined and abandoned sites. This project summary describes a background report on the hydrology, mineralogy and ground water chemistry of the Green River Formation in the Piceance Basin. The full report comprehensively discusses what is known about the three physico-chemical systems which will interact to produce ground water quality variations at an uncontrolled mine site in the Piceance Basin and more specifically, at either of the two federal lease tracts Ca and Cb situated therein.

This Project Summary was developed by EPA's Robert S. Kerr Environmental Research Laboratory, Ada, OK, to announce key findings of the research project that is fully documented in a separate report of the same title (see Project Report ordering information at back).

#### Introduction

The Green River Formation underlies an area of approximately 6,500 square kilometers (17,000 square miles) in Wyoming, Utah, and Colorado and contains an estimated 1.8 trillion barrels of oil and shale beds. Structurally, it occurs in seven basins - the Uinta, Piceance, Sand Wash, Washakie, Green River, Great Divide, and Fossil basins. Stratigraphically, the formation generally thickens toward basin centers, and laterally inter-tongues and is interbedded

with adjacent units toward basin margins. Sedimentologically, it represents deposits of two large Eocene lakes, Gosiute and Uinta, in which oil-bearing shales associated with beds of tuff, siltstone, claystone, sandstone, halite, trona and nahcolite were deposited. In total thickness, it may exceed a few thousand meters, and in places it is saturated by ground water throughout its entirety.

Modified in situ (MIS) processes of extraction of oil from Green River shales has received much attention as a potential method of retorting. The MIS method is advantageous because shale extraction costs are reduced, deeper shale beds can be retorted, less water is required, and less surface disturbance occurs from spent shale and retorting processes. However, the dewatering of the mining zone and the chemical and mineralogic alteration of it during in situ retorting will change the local ground water regime.

Alteration of ground water flow rates and volumes, and changes in ground water chemistry will certainly result from an MIS burn. In addition, changes in local mineralogy will occur dependent upon changes in quantities, rates and directions of water moving through the MIS system. A new equilibrium of ground water quality will be established after retorting. Accordingly, the purposes of this report are: 1) to review the existing knowledge regarding the potential effects of the MIS process on properties of ground water storage and flow in the Green River Formation, 2) to review the existing knowledge of the mineralogy of the Green River Formation, and 3) to review the existing knowledge of possible mineral-ground water interactions during and after an MIS event.

#### Modified In Situ Technology

This section discusses modified *in situ* (MIS) technology with major emphasis on leaching and ground water quality. The approximate size of one *in situ* retort will be 50 meters by 50 meters laterally and 300 meters vertically.

The MIS process consists of two basic steps. The first involves forming the in situ retort by removing about 20 to 40% of the oil shale deposit from the bottom of the column to be retorted and expanding by sequential explosions the remaining shale into the void volume. The second step is retorting the rubblized oil shale in place. The heat required for pyrolysis is supplied by either external or internal means and the volatilized oil is condensed and collected by means of a sump below the retort and pumped to the surface. The shale oil is in the form of condensable hydrocarbon vapors which is cooled to produce a semi-viscous liquid. Along with this, noncondensable vapors such as methane, CH<sub>4</sub>, and ethane, H<sub>3</sub>C-CH<sub>3</sub>, are produced along with other hydrocarbons and organic compounds which exit with the off-gas. A considerable volume of retort water is also collected with the oil. The retort water comes from the liberation of free and bound water from the oil shale maxtrix; the combustion of hydrocarbons, the dehydration of various oxygencontaining compounds, and the recombination of  $H^{+}$  and  $OH^{-}$  ions which are produced during pyrolysis.

Pyrolysis is defined as thermal decomposition in the absence of oxygen. As already mentioned, pyrolysis in an in situ retort is supplied by external or internal means. Use of an external heat source requires the pumping of a hot inert gas such as nitrogen through the retort. As the pyrolysis zone moves, a zone of spent shale containing organic residue is left behind. When this alternative is used, the reducing conditions exist throughout the retort. Use of an internal heat source implies the combustion of residual organics on the shale as the heat source for pyrolysis. The shale is initially ignited with propane, and air is then continuously supplied to the retort. The result is the formation of a pyrolysis zone and a combustion zone. The pyrolysis zone moves in front of the combustion zone leaving behind some organic matter which serves as fuel for the combustion zone. Behind the combustion zone is the spent shale. In this type of retort both oxidizing and reducing conditions exist at the same time, but for convenience the overall environment of the retort is defined as being oxidizing. Some of the residual carbon from this process still remains on the spent shale.

The MIS process will result in alterations of the ground water regime different from those obtained from traditional underground mining and surface retorting processes. Specifically, changes in the types and distributions of permeability and thus the rates and volumes of flow will result. These changes, together with the altered chemical and mineralogic composition of the mining zone, will in turn affect the final chemical quality of the ground water.

#### Hydrology

Although investigations have been made of the chemical and flow properties of ground water in the oil shale basins, a thorough assessment of the effects of the modified *in situ* process has not been accomplished, principally because of its quite recent development as an important process. However, it is apparent that underground changes in mineralogy and water chemistry will be fewer for standard methods as compared to the modified *in situ* process.

Existing models of oil shale basins and their ground water systems are regional in scope and emphasize dewatering rates and effects of underground mining processes. Such models, constructed and calibrated for the hydraulics of intergranular permeability, may apply over large areas, but are not the best predictors of the local effects of changes from initial conditions of secondary (fracture and/or solution) permeability to rubbilize intergranular permeability, as will occur during the MIS retort process. And finally, no models in existence consider ground water quality equilibria and their responses to mining in conjuction flow properties in the oil shale environment. Models including processes of hydrodynamic dispersion and hydrogeochemical attenuation in fracture flow systems are applicable in solving these problems.

Because approximately two-thirds of the oil shale potential of the Green River Formation exists in the Piceance basin in Colorado and because initial steps are underway to recover oil using the MIS process at both Colorado federal lease tracts Ca and Cb, these areas will be emphasized.

### Ground Water in the Piceance Basin

The richest oil shale in the Piceance Basin is in a layer known as the Mahogany zone. In much of the Piceance Basin it acts as an aquitard restricting the

movement of ground water between two major aquifer systems, one above and another below the Mahogany zone. The upper aguifer includes the Uinta Formation (formerly called the Evacuation Creek member), and the upper strata of the Parachute Creek member of the Green River Formation, consisting chiefly of oil shale. The lower aguifer is the section of the Parachute Creek member below the Mahogany zone. The garden Gulch and Douglas Creek members, beneath the Parachute Creek member, are like the Wasatch formation below them. They all consist of clay, shale, and lenticular sandstone beds. (Figure 1)

Units below the Parachute Creek member are not aquifers in the Piceance Basin. Some alluvial deposits along stream channels are aquifers, but will be affected only indirectly by MIS retorting; thus they will not be considered here.

As of 1979, over 100 exploration or ground water sampling, testing and/or monitor wells had been drilled in the

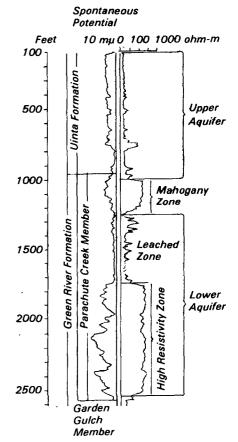


Figure 1. Electric log response showing stratigraphic units and aquifer designation according to the USGS in the Piceance Basin (From Welder and Saulnier, 1978, p. 4).

Piceance Basin. Approximately 30 wells exist at each Federal lease tract, Ca and Cb, with nearly as many additional wells nearby. Many of the exploration wells were drilled through both aquifers and still permit the exchange of water between them. However, programs of well recompletion for testing and/or monitoring have recently been initiated.

The detailed testing of aquifers at Tracts Ca and Cb have resulted in the identification of three aquifers at Tract Cb and two at Tract Ca.

#### Lower Aquifer

The major individual bedrock aquifer in the Piceance Basin is the lower aguifer (leached or low resistivity zone). Primarily, it has secondary permeability, like that of both the Mahogany zone and the upper aquifer. In addition, its fracture permeability has been enhanced by the solution of nahcolite and other minerals. Its transmissibility is highly variable and may reach 250 m<sup>2</sup>/day (2600 ft<sup>2</sup>/day). In contrast, during pumping tests of individual horizons in the lower aquifer at Tract Cb, low transmissibilities from 0.15 to 8.5 m<sup>2</sup>/day (1.6 to 92 ft<sup>2</sup>/day) were obtained. Storage coefficients of the lower aquifer in such tests have ranged from 10<sup>-3</sup> to 10<sup>-1</sup>

The variation in transmissibility is a result of the pronounced anisotropy of permeability of the aquifer, which is primarily due to the orientation of fracture systems (both faults and joints) and variations between different oil shale beds. In addition, the preferred orientation of faults and folds, in northwest, southeast, and east directions, undoubtedly has a significant effect on ground water movement.

#### Upper Aquifer

The upper aquifer has chiefly fracture permeability, with little evidence of significant solution permeability. Its transmissivity ranges up to approximately 9 m²/day (1,000 ft²/day) and generally increases from east to west in the basin. Most investigators have noted that hydraulic coefficients of the upper aquifer also vary widely within small distances. In general, however, the upper aquifer is less permeable than the lower. Of course, the upper aquifer is not confined everywhere in the basin. It will have to be dewatered to retort oil shale by the MIS process.

#### **Ground Water Movement**

Studies of wells penetrating both the upper and lower aquifers have shown distinctly different water levels between them. In general, potentiometric heads

are higher for the upper aquifer in recharge areas and higher for the lower aquifer in discharge areas. Head differences commonly vary between 15 and 30 meters. The results indicate that the ground water system is recharged at higher elevations near the basin margin on the south, and that discharge from the ground water system to the streams occurs near the basin center and to the north along White and Yellow Creeks.

### Mineralogy of the Green River Formation in Piceance Basin

The Eocene Green River Formation. host to the rich oil shales of the Piceance Creek Basin, has long been of interest to mineralogists due to the occurrences of rare and unusual minerals within its strata. In the past 50 years, hundreds of studies have been carried out by researchers on core cuttings and cores from the Piceance, Uinta, Green River and Washakie Basins in Colorado, Wyoming and Utah. Studies, discussed in the full report build up a picture of an amazingly diverse formation composed of authigenic carbonates, silicates, sulfides, sulfates, halides, oxides, hydroxides, phosphates and hydrocarbons in a highly stratified sequence of sediments covering over 16,000 square miles of a three-state area and representing the single largest oil resource known in the United States.

The Green River Formation in the Piceance Basin of northwestern Colorado is generally subdivided into three members and include the lowermost Douglas Creek Member, which is stratigraphically equivalent to the Anvil Points Member in parts of the basin, the Garden Gulch Member, which in places in time-equivalent to the underlying and adjacent Douglas Creek and Anvil Points, and the uppermost Parachute Creek Member, host to the rich oil shales of the basin.

Together these units form a complexly interfingered series of sandstones, siltstones, mudstones, shales, oil shales, limestones, marlstones, and evaporites with occasional tuff beds.

The deposits in the Piceance Basin were laid down beneath the waters of Eocene Uinta Lake. The Douglas Creek Arch undoubtedly formed a barrier to communication between the Uinta and Piceance basins during periods of low water in the history of Lake Uinta, thus it is not surprising that the beds of the Green River Formation in the Piceance Basin are mineralogically distinct from those of the Uinta Basin.

Generally speaking, the evaporites (halite and the sodium carbonates) were laid down during dry periods in the

deepest parts of the section of Lake Uinta, which occupied the Piceance Basin. During wetter periods the marlstone and organic-rich oil shales accumulated.

The distinguishing feature of the Piceance Basin is its relatively simple mineralogy in comparison to the Uinta and Green River-Washakie Basins. The Green River beds in the Piceance Basin have been extensively characterized due to the rapid development of oil shale industries seeking to mine in the area. This is especially true of the Parachute Creek Member, which contains the Mahogany zone oil shales, the main oil shale ore of the basin. A report on all the studies carried out on the mineralogy of the oil shales of the Piceance Basin alone would form a document of formidable size.

### Ground Water Chemistry of Piceance Basin

This section of the full report describes the major types of chemical reactions occurring in the aguifers of the Piceance Basin with consideration given to the specific mineral assemblages. The concentration of dissolved solids in the aguifers of the Piceance Basin varies over 2 orders of magnitude with values of 400 mg/l at the margins of the basin and up to 40,000 mg/l in the North Central part of the basin. Along with these lateral changes, there are also changes in concentration with depth. These changes in water quality include an increase in dissolved-solids concentration, a change in water type from a mixed cation bicarbonate water to a sodium bicarbonate type, oxidation and reduction of sulfur species, and relatively large increases in certain trace constituents such as strontium and fluoride. These changes reflect the geochemical environment through which the ground water flows and that the magnitude of the changes is affected by the type and concentration of soluble minerals present in the aquifer, the type of clay minerals and the amount of organic material present in the aquifers, and finally, the flow path of the water through the aquifers.

As the ground water of the upper aquifer flows from the recharge areas, the TDS concentration increases and the water changes to a sodium bicarbonate, NaHCO<sub>3</sub>, type. Large increases in TDS concentrations occur in the Uinta Formation where concentrations of two to three times that of the recharge zone are observed. Also, near the base of the upper part of the Parachute Creek member, TDS concentrations are up to ten times that of the recharge water. The principal source of this increase is upward flow of water

with a high dissolved solids concentration from the lower aquifer to the upper aquifer. Upward flows also probably account for the larger dissolved solids concentrations near Tract Cb and in the north-central discharge areas of the basin.

# Trace Elements in the Green River Formation of Piceance Basin

A knowledge of the trace element distribution is important so that leachability can be appropriately modeled. Relative to average rocks, shale contains much higher levels of selenium and arsenic, and moderately higher levels of cobalt, nickel, chromium, zirconium, and manganese, cadmium, antimony, mercury, fluoride, and boron.

#### Conclusion

The final report is a compilation of the general state of knowledge of environmental chemistry in oil shale research. It offers no conclusive definitions on the leaching phenomenon from MIS retorts. Some trends can be seen in the various investigations; however, the available data can only be classified as preliminary. Completed investigations on inorganic leachables are not in agreement with one another, and there has been only one effort with organic leachables. Completed work does point out which parameters warrant further study.

The major tool which will be required to complete the chemistry for this project will be a geochemical computer model which simulates mass transfer and reaction path sequences among a given mineral assemblage. Once the mineralogy of spent shale is known in detail, the geochemical computer model can predict the

changes in water quality, and knowledge of hydrology can show the flow path of the leachables.

J. J. Fitzpatrick is with the University of Denver, Denver, CO 80208.

B. D. Newport is the EPA Project Officer (see below).

The complete report, entitled "Ground Water—Mineralogy Relationship for In Situ Oil Shale Retorting," (Order No. PB 84-187 764; Cost: \$46.00, subject to change) will be available only from:

National Technical Information Service

5285 Port Royal Road

Springfield, VA 22161

Telephone: 703-487-4650

The EPA Project Officer can be contacted at:

Robert S. Kerr Environmental Research Laboratory

U.S. Environmental Protection Agency

P.O. Box 1198

Ada, OK 74820

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U S ENVIR PROTECTION AGENCY
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230 S DEARBURN STREET
CHICAGO IL 60604